Spectro-Electrochemistry of Silicon Model Electrodes

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2018 Annual Merit Review

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Project ID# BAT346

Overview

Timeline

- October 1st 2016 - September 30st 2019
- Percent complete: 40%

Barriers Addressed

- Development of PHEV and EV batteries that meet or exceed the DOE and USABC goals
  - Cost, Performance and Safety

Budget

- FY18 funding $3900K

Partners

- Five Laboratory Team lead by NREL:
  - Sandia National Laboratory
  - Argonne National Laboratory
  - Oak Ridge National Laboratory
  - Lawrence Berkeley National Laboratory
- UC Berkeley
- Colorado University Boulder
- Colorado School of Mines
- University of Rhode Island

Relevance : Objectives

1. This collaborative project involves fundamental research efforts to tackle the barriers associated with development of an advance lithium ion negative electrode based upon silicon as the active material.
   - Baseline model systems also include SiO_x, Sn and Ge, and their alloys.
2. Understand and eliminate fundamental scientific and technical limitations to implementation of a silicon based anode in commercial cells
   - Address the inherent non-passivating behavior of silicon and intermetallic electrodes in organic electrolytes, which results in large irreversible capacity loss and gradual electrolyte consumption during the electrode operation.
3. A better understanding of the underlying principles that govern these phenomena is inextricably linked with successful implementation of high energy density materials such as Si in Li-ion cells for PHEVs and EVs.

Milestones FY18

Quarter 1 Milestone:

Have completed the selection and characterization (XPS, SIMS, IR, and Raman), including determination of the surface termination chemistry and impurity levels, of the SEISta model research samples to be used by all members of the team in FY18. **100% complete**

Quarter 2 Milestone:

Have characterized (XPS, SIMS, IR, and Raman) the surface chemistry and composition of the SEISta model research samples after contact with the electrolyte, before cycling, including the nature of the electrolyte decomposition products. **100% complete**

Quarter 3 Milestone:

Completed characterization (electrochemistry, IR and Raman) of the early stage silicon electrolyte interphase formation on the SEISta model research samples, specifically by establishing and demonstrating a procedure for quantitatively measuring the solubility of SEI on silicon surfaces. **In progress**

Quarter 4 Milestones:

Established and demonstrated a procedure for measuring the growth rate of silicon SEI components at fixed potentials and during cycling. **In progress**

Have determined how the physical properties of the silicon electrolyte interface are influenced by the nature of the silicon surface on the SEISta model samples. **In progress**

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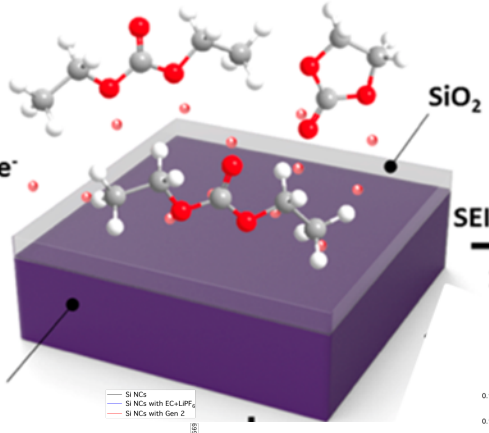
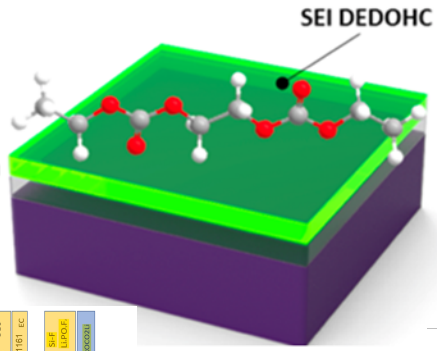
Chemical Reactivity vs. Electrochemical Reactivity of Si



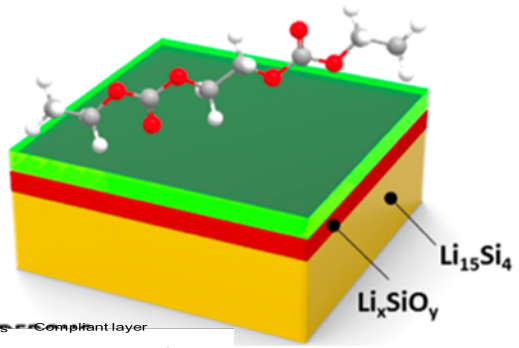
SEI formation

1.3 V

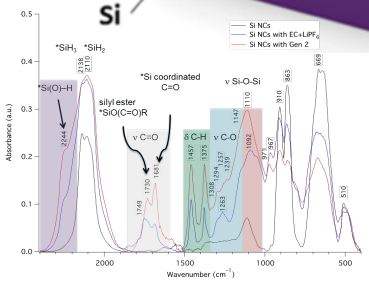


Lithiation

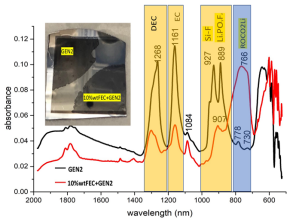
0.1 V



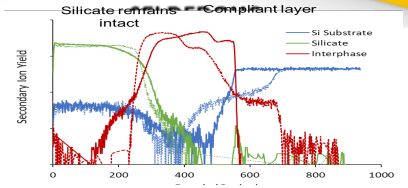
J. Phys. Chem. C 2017, 121, 14476−14483



Chemical Reactivity of Silicon, ID BAT345

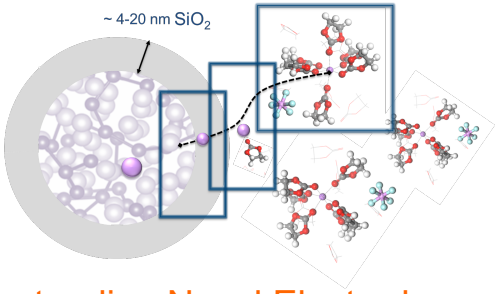


Surface analysis of the Silicon SEI, ID BAT347

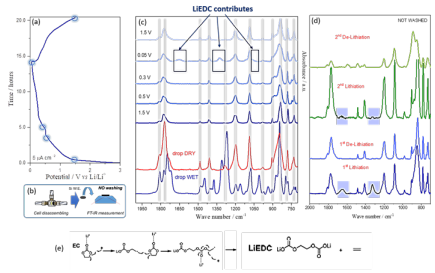


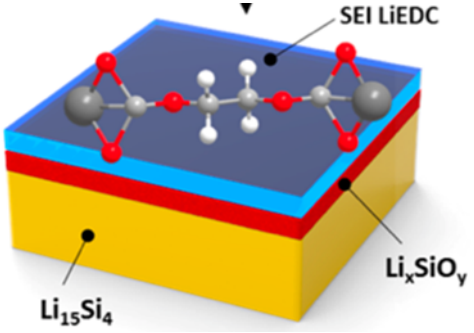
Role of Li Silicates in Si SEI Formation, ID BAT348

Spectro-electrochemistry of Si, ID BAT346



Predicting and Understanding Novel Electrode Materials From First-Principles, ID BAT344





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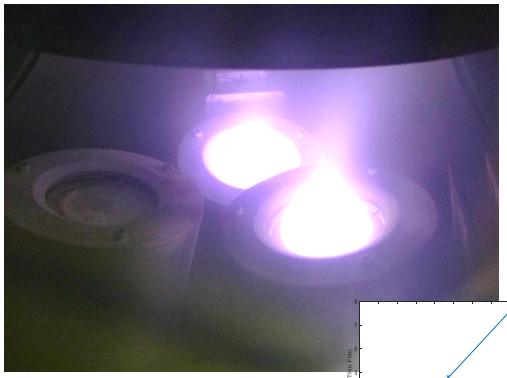
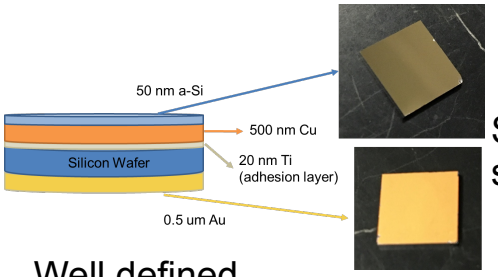
Diagnostic Evaluation of Model Si Anodes

Approach

- Standard Si substrates
  - 50 nm silicate/50 nm Si/500 nm Cu/650 um D-Si/500 nm Au
  - Samples from Gabe Vieth, ORNL (BAT 345)
- Sputter ***model thin-films*** to obtain ***controlled composition and structure***
- Coordinate testing and characterization efforts
  - Use consistent and reproducible experimental methodologies
  - Standardize electrochemical test cells
  - Cell design from Rob Kostecki, LBNL (BAT 346 and Chunmei Ban, NREL (BAT 347)
- Electrode surface characterization using SIMS/ XPS/ATR-FTIR/ECAFM
- Correlating the mechanism of interfacial phenomena with the electrochemical performance of the Si electrode

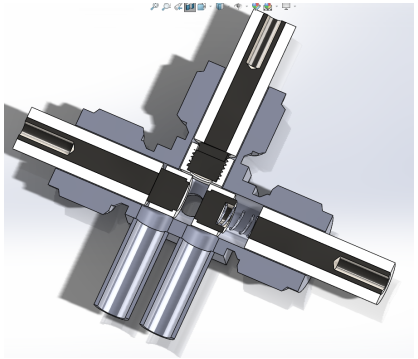


ACS, PVD for composition control



Standard samples

Well defined architectures

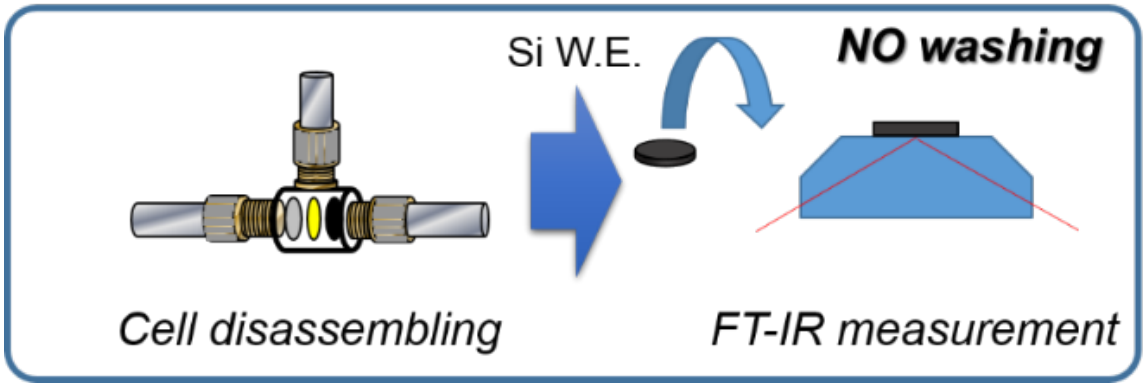


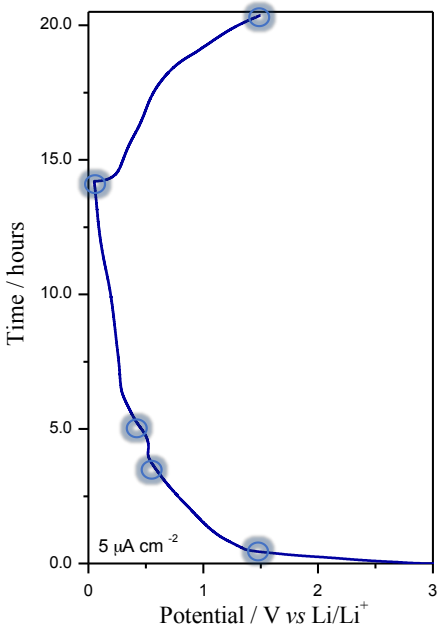
Testing protocols

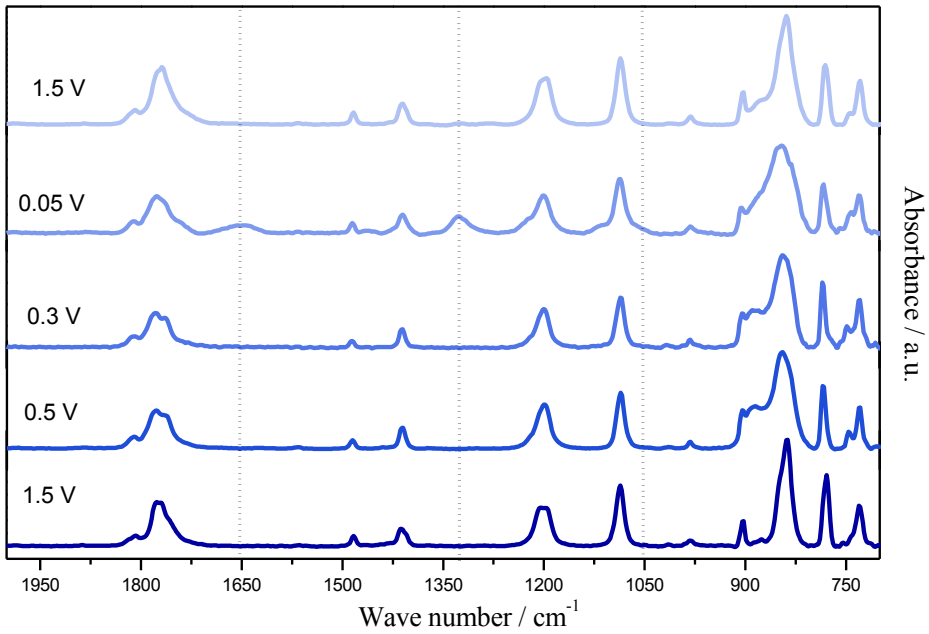
Electrochemical Reactivity of Si Thin-Film

Ex situ FTIR Analysis of Cycled Si Electrodes

3 electrode cell, E_{ref}, E_c- Li-foil
T=25°C , current density: 5 μA cm^{-2}
1.2M $LiPF_6$, EC:EMC 3:7 wt.%



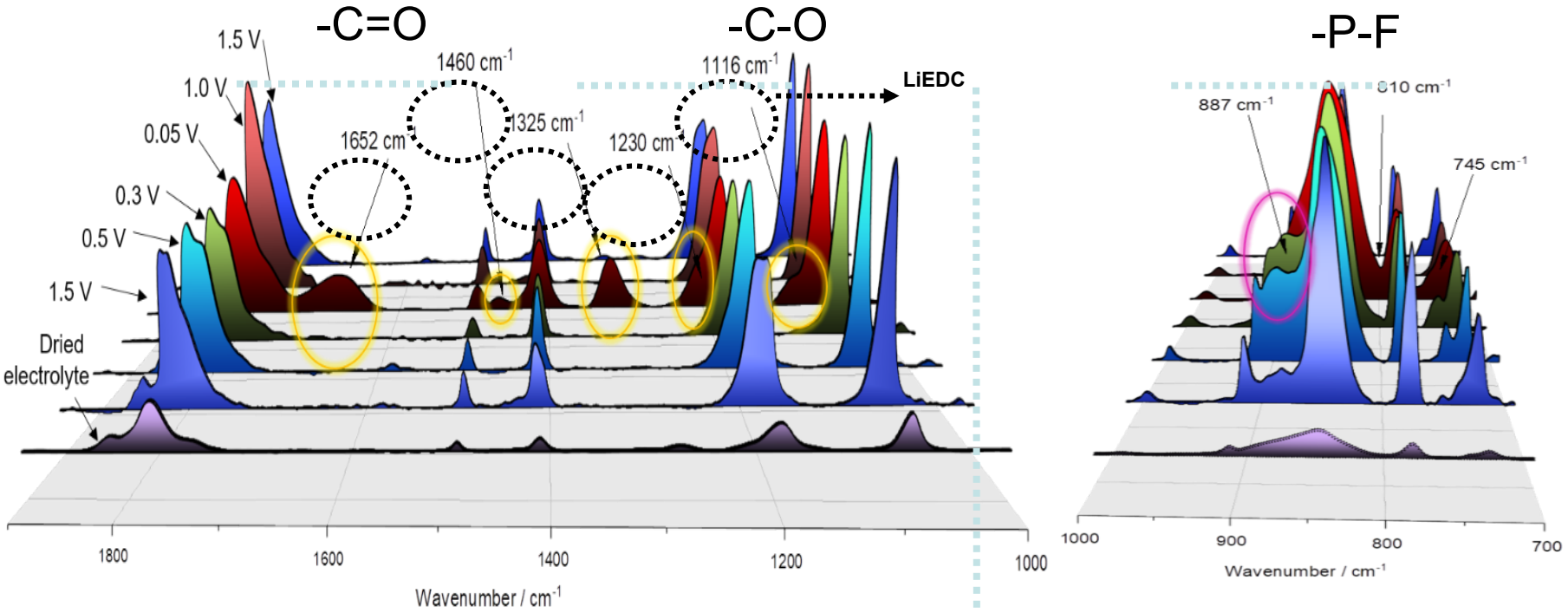




- FTIR spectra of the Si electrode show only minor variations upon polarization.
- Detailed peak deconvolution and assignment is necessary to assess these changes.

Ex Situ ATR FTIR Study of Thin-Film Si Anode

1st lithiation/delithiation



- New IR bands at 1652, 1460, 1325, 1230, 1116 cm^{-1} appear at low potentials (0.05 V) and then disappear upon delithiation.
- Increasing concentration of (P-F)-containing compounds is observed.
- New spectral features appear at 745 and 810 cm^{-1} in the fully lithiated state, which also decrease upon delithitaion.

Lithium Ethylene Dicarbonate in the SEI Layer

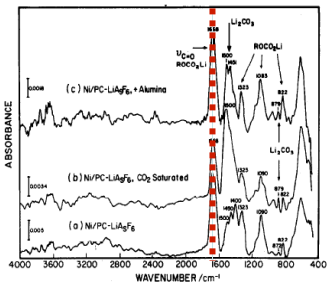
Earliest FTIR studies of surface films on metallic Li in ethers, PC and EC were performed by *Aurbach et al. J. Electrochem. Soc., 1987; J. Electroanal. Chem., 1992; J.Electrochem.Soc., 1994*

Suggested EC reactions on metallic lithium:

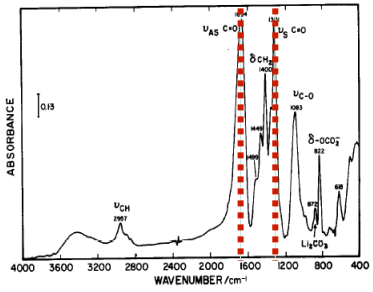
$$2EC + 2e^- + 2Li^+ \rightarrow (CH_2OCO_2Li)_2 + CH_2{=}CH_2 \uparrow$$

Reduction path and product referred primarily to 1640 cm^{-1} peak in LiEDC. In fact it was probably lithium ethyl carbonate. Analyses were primarily from electrolysis products isolated from solution (not surface) and "chemical intuition".

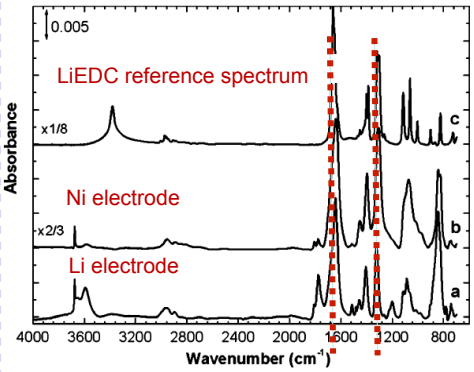
Nickel electrodes polarized to 0 V (Li/Li+) in PC + $LiAsF_6$



Electrolysis product of EC in THF+0.5 M TBAP on gold, isolated as Li salt

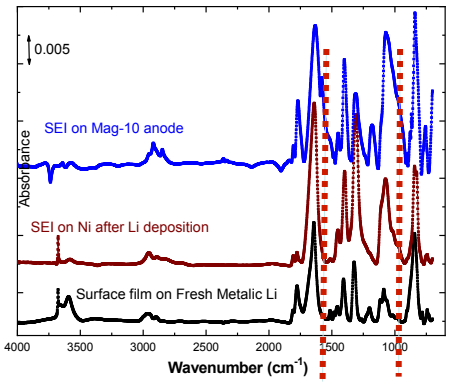


Ross et al.. J. Phys. Chem. B, 2005



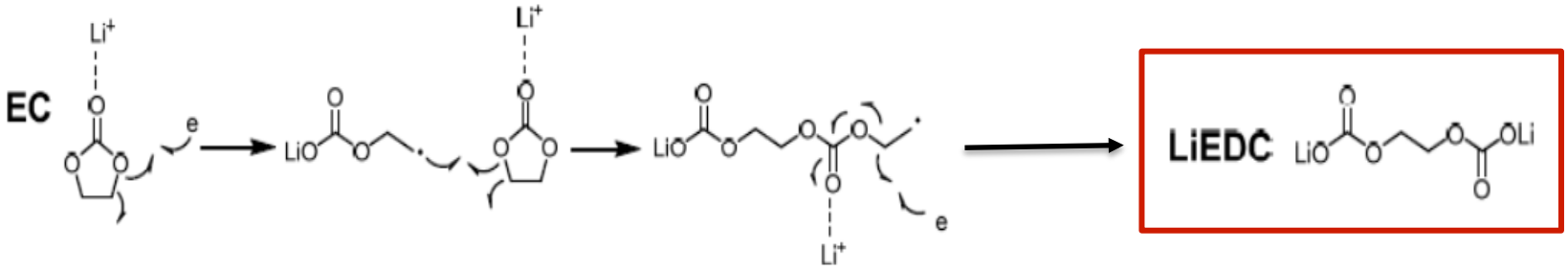
EC decomposition on Li and Ni electrode leads to formation of LiEDC.

Ross et al., Electrochem. and Sol. State Lett. 2005



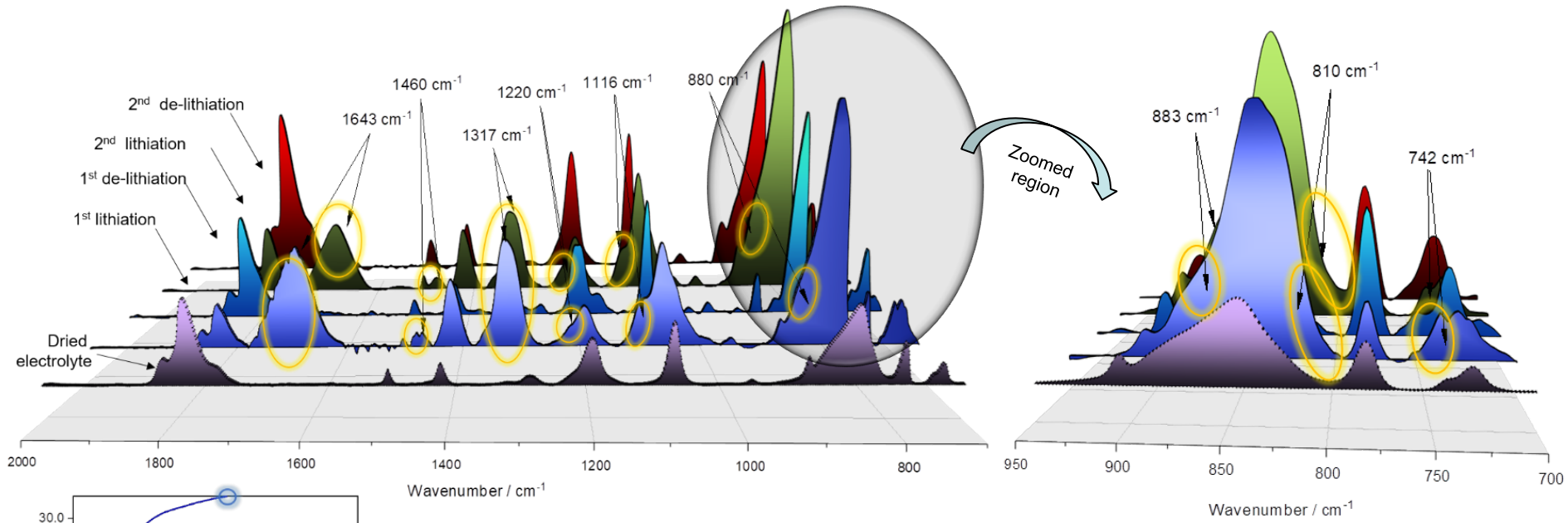
LiEDC (and other components) is also observed in the SEI layer on Graphite.

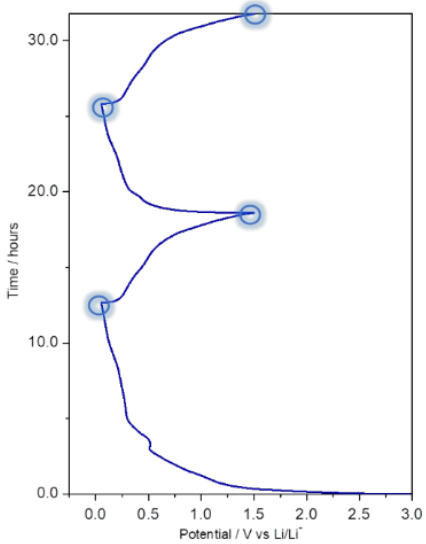
- *LiEDC universally forms in EC-containing electrolytes at different electrodes such as Ni, Li, Graphite and Si.*
- *Is LiEDC the essential component of the SEI layer?*



Ex Situ ATR FTIR Study of Thin-Film Si Anode

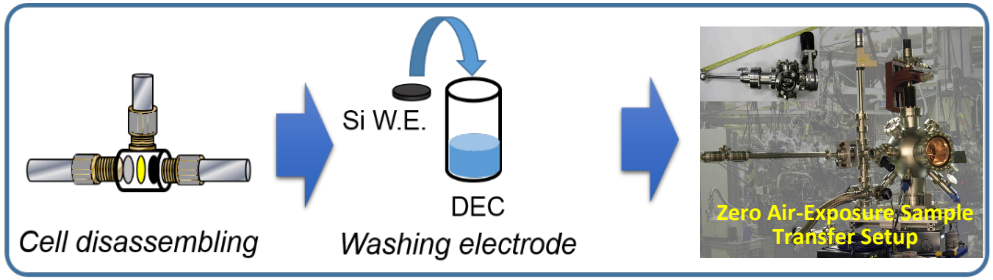
1st and 2nd lithiation/delithiation

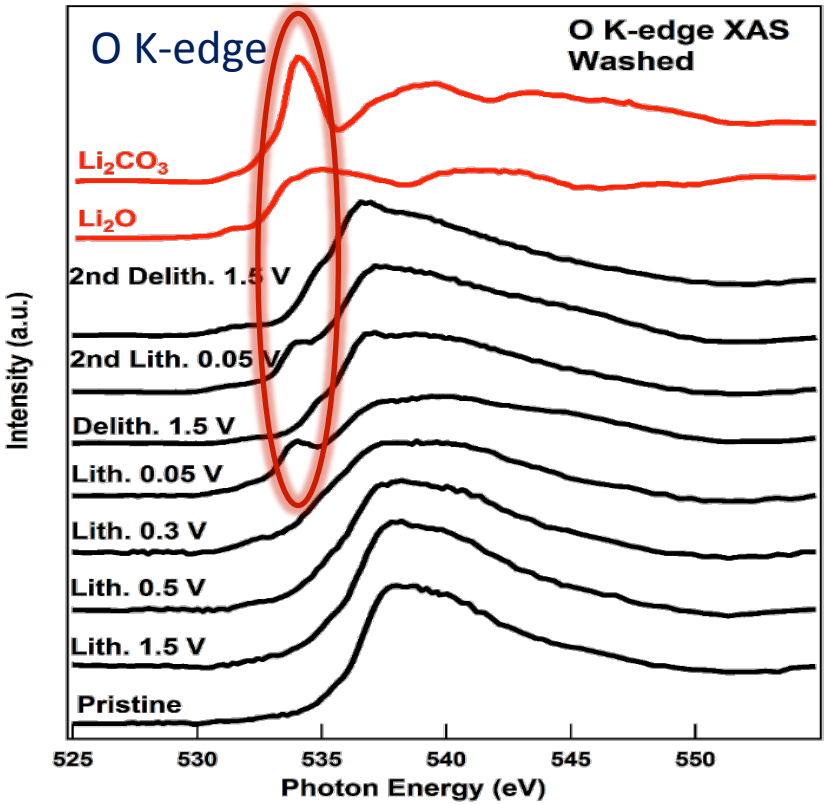


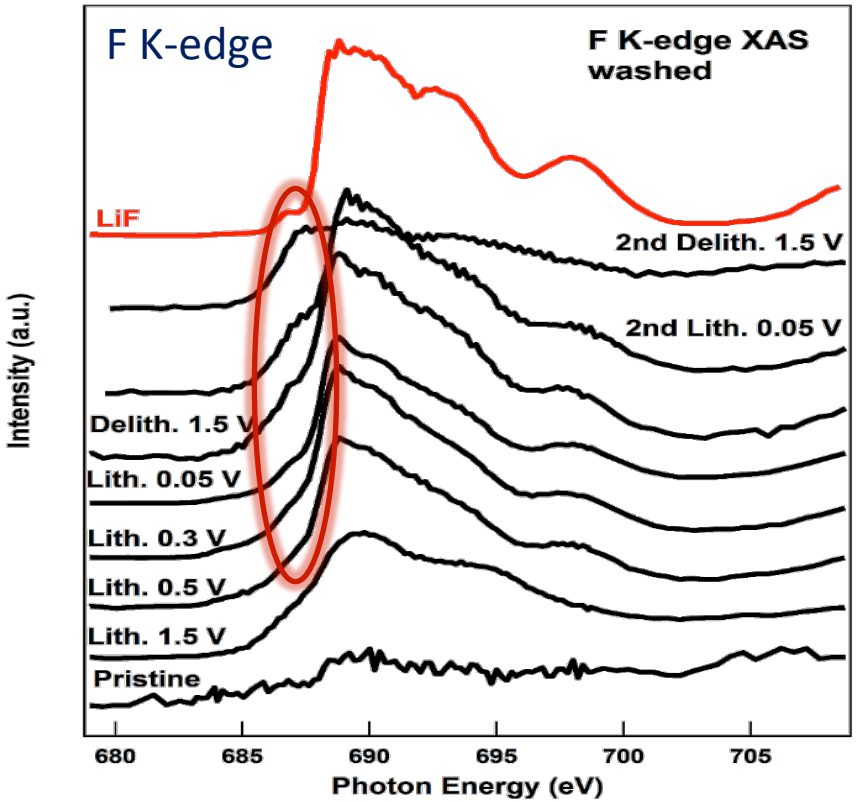


- LiEDC forms during 1st lithiation at low potentials (0.05 V) and it disappears during delithiation process.
- LiEDC re-appears during 2nd lithiation and then disappears again upon de-lithiation.
- Intensity of peaks at 745 and 810 cm^{-1} also vary during cycling.
- Gradual increase of (-P-F)-containing compounds is observed.

Ex situ XAS of Si Thin-Film Electrode





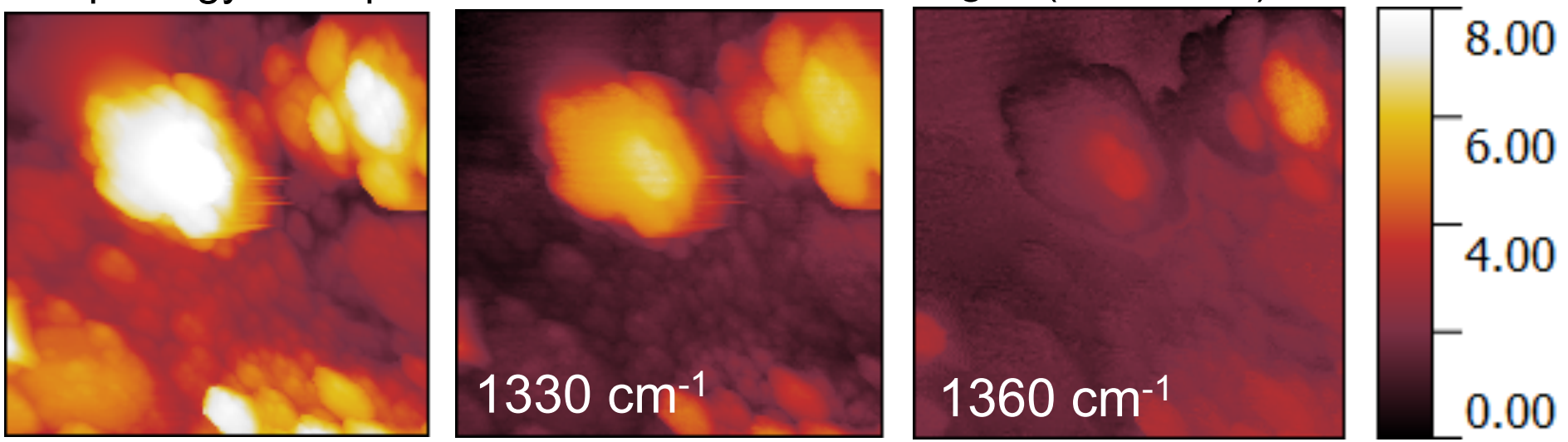


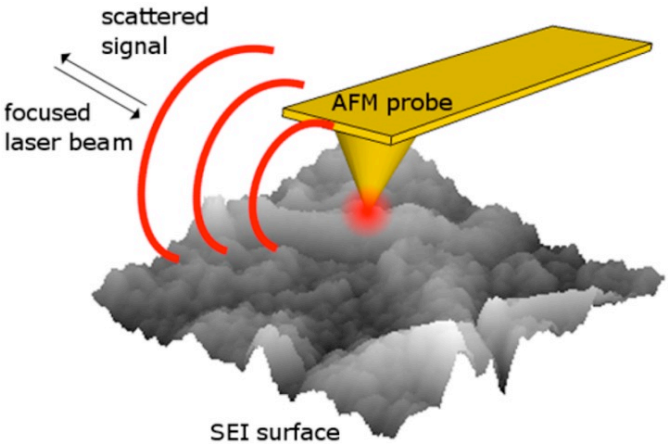
- No reference XAS spectra of LiEDC. The peak at 533 eV can originate from LiEDC
- LiF is omnipresent in the film during1st cycle. More F-containing species appear at the end of 2nd cycle.

Ex situ Near-Field IR Imaging of Si Electrode

Morphology 5 x 5 μm

IR absorbance images (O2 Phase)



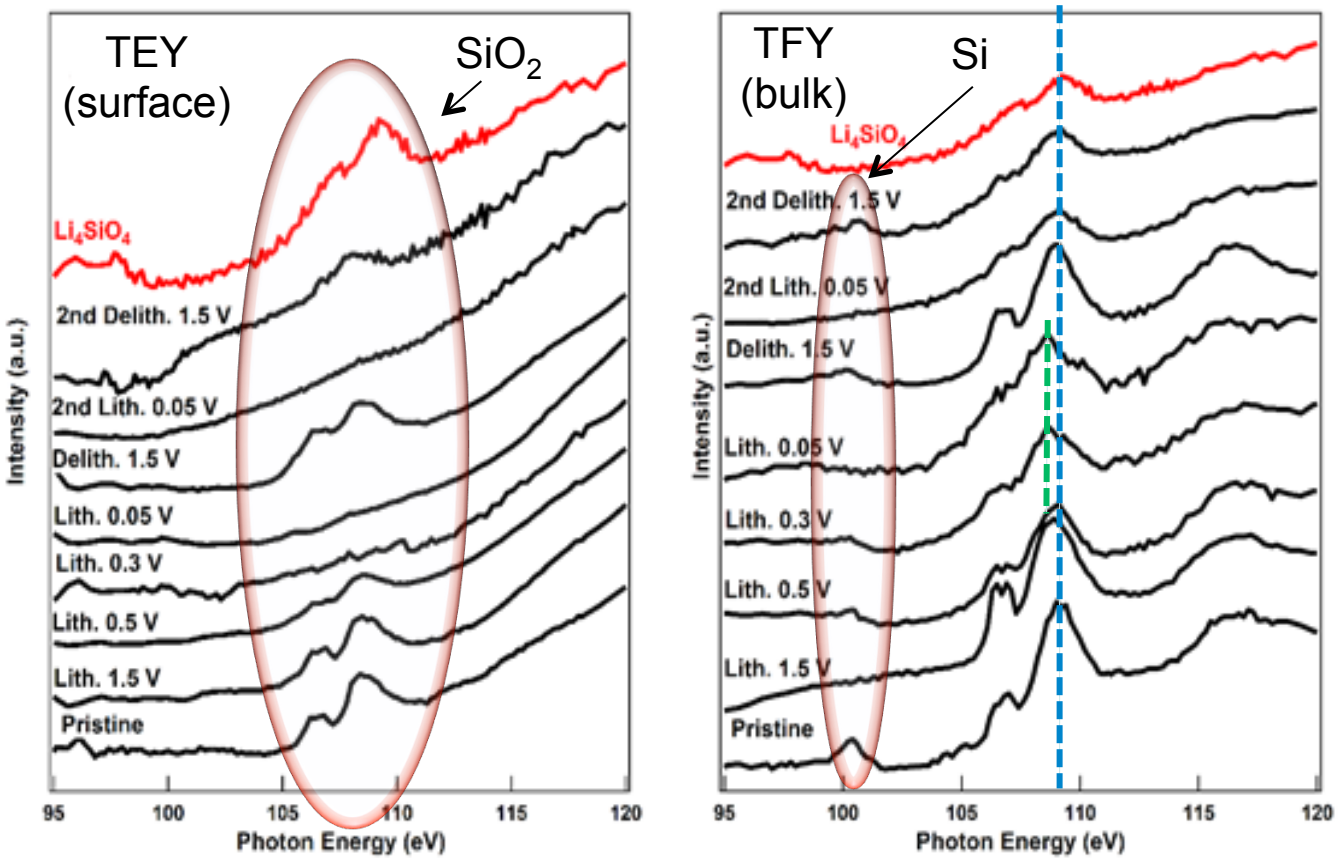


- Single wavelength Infrared near-field scanning optical microscopy was applied to investigate the SEI on Si thin-film electrode at 0.05 V. ,
- NFIR allows to resolve structure, composition and distribution of individual components in the SEI at nm resolution.

NFIR imaging at 1330 cm^{-1} reveals large clusters of LiEDC scattered at the surface of the silicon electrode

Ex situ XAS of Si Thin-Film Electrode

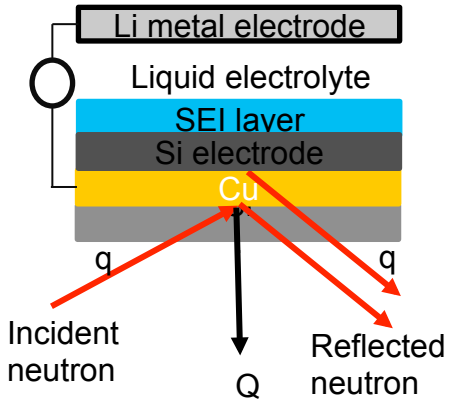
Si L-edge

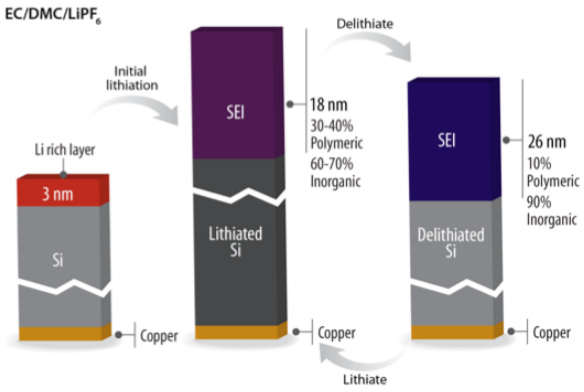


- XAS TEY signal from SiO_2 disappears during at 0.05 V and then reappears at 1.5 V. Thickness of the SEI layer increases upon lithiation and decreases during delithiation.
- XAS TFY SiO_2 peaks positions and their relative intensity vary upon lithiation/ delithiation. Possible reversible formation of Li_xSiO_y solid solution.

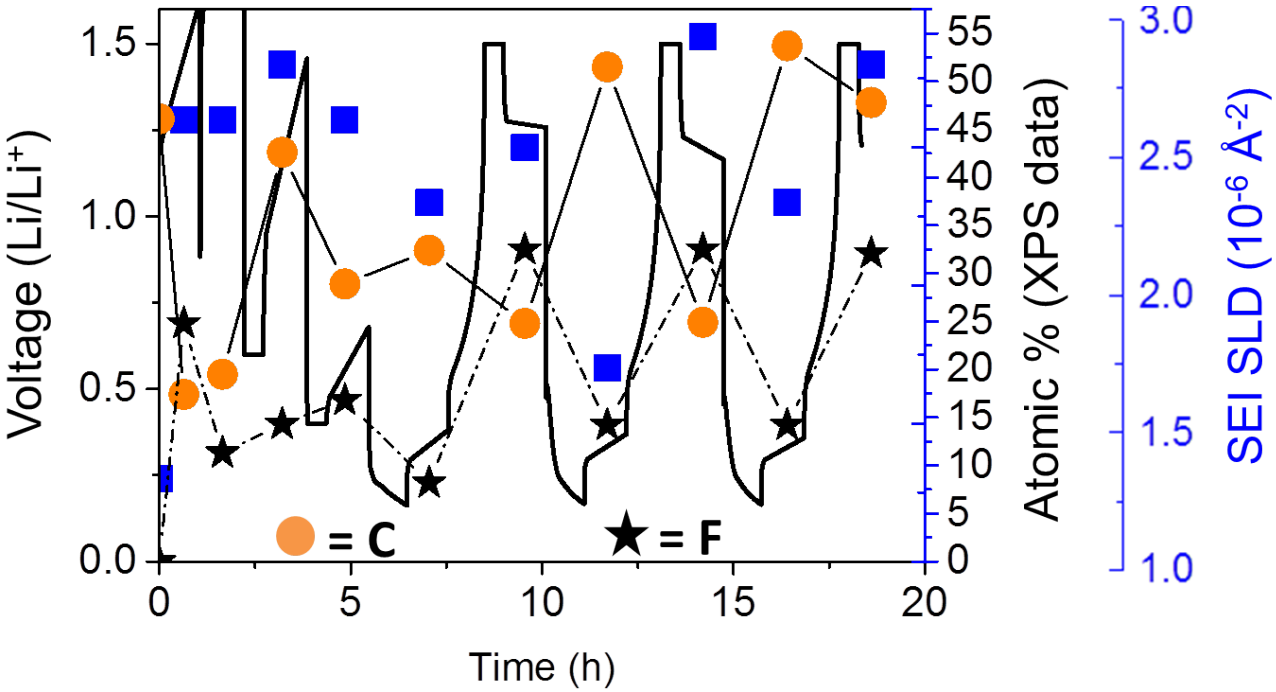
In situ Neutron Reflectometry *of* Si Thin-Film Electrode

Work carried out by G. Veith, ORNL. Please see BAT345





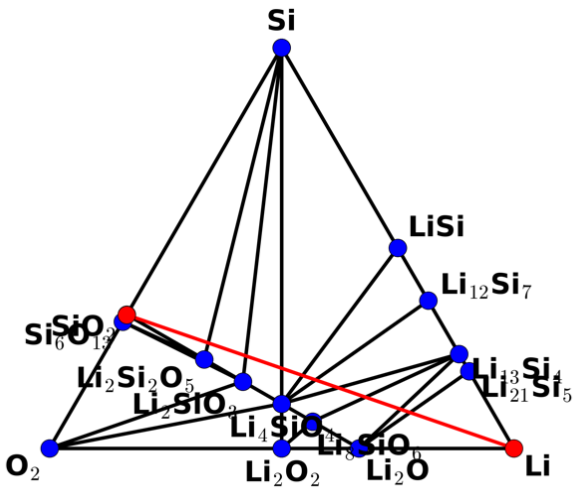
Veith et al., Nature Scientific Reports 2017



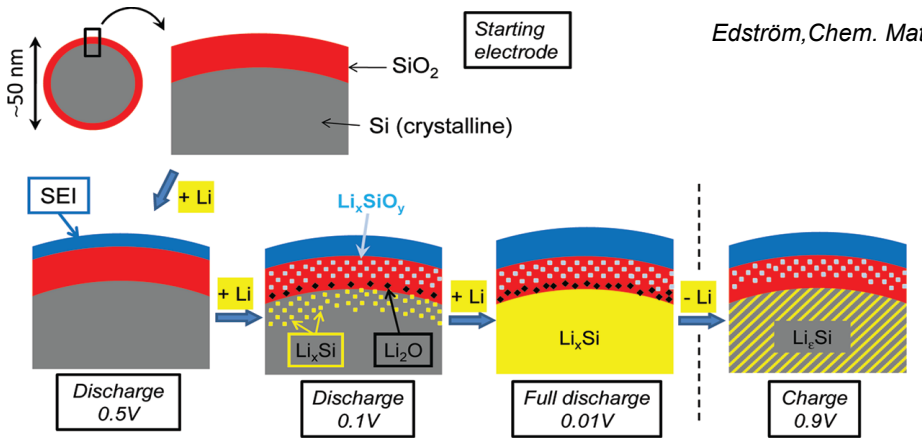
- Thickenss and composition of the SEI changes with SOC – Li/organic at low voltages, inorganic during delithiation
  - Data shows at full lithiation the SEI is dominated by organic species
  - Delithiated the SEI is dominated by inorganic species due to loss of organic component – *could be LiEDC based on scattering length densities*

Interfacial Instability of Si Anodes

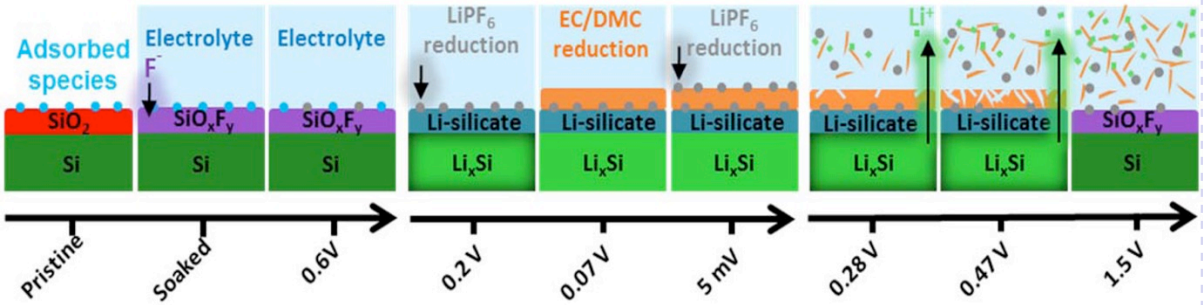
Persson, int comm. 2018 LBNL



Edström,Chem. Mat 2012

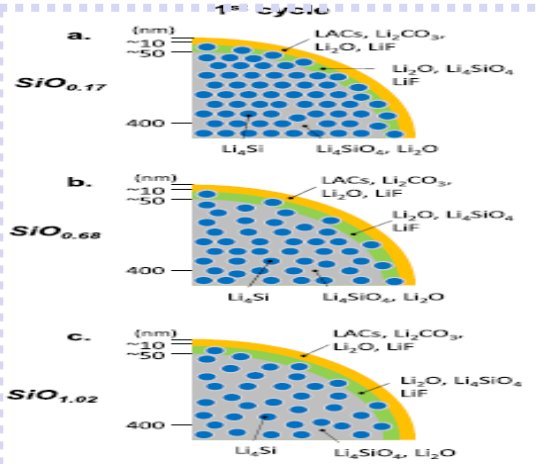


Schematic view of the mechanisms occurring at the surface of silicon nanoparticles. Formation of the SEI at the beginning of discharge. Formation of the Li−Si alloy upon further discharge, together with Li2O and LixSiOy interfacial phases. Partial reversibility upon charge.



Scheme of the proposed reaction mechanisms occurring during the early cycling of an amorphous Si thin film in LP30 liquid electrolyte.

Novak, ACS Appl. Mater. Interfaces 2016

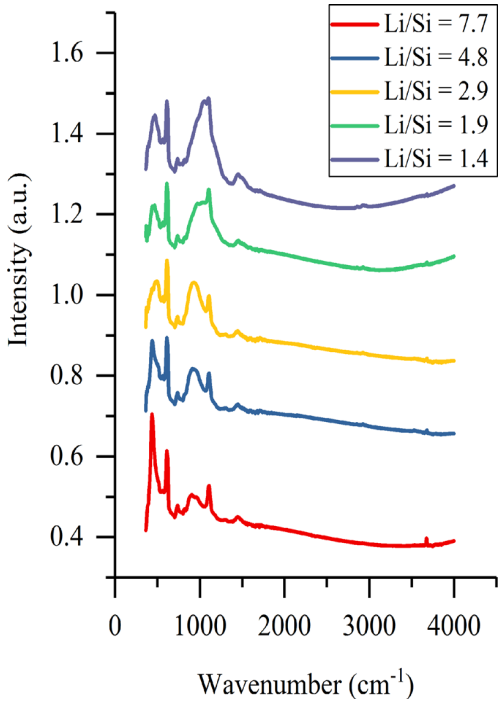


Abe, Electrochimica Acta 2017

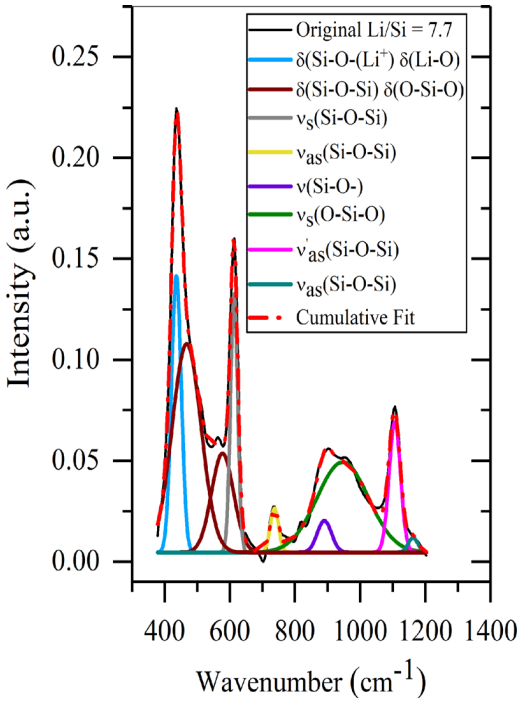
The SEI layer and electrolyte are subject to continuously evolving surface reactivity via changes of structure and composition of Li_xSi and Li_xSiO_2.

Silicates in the SEI Layer of Si Anodes

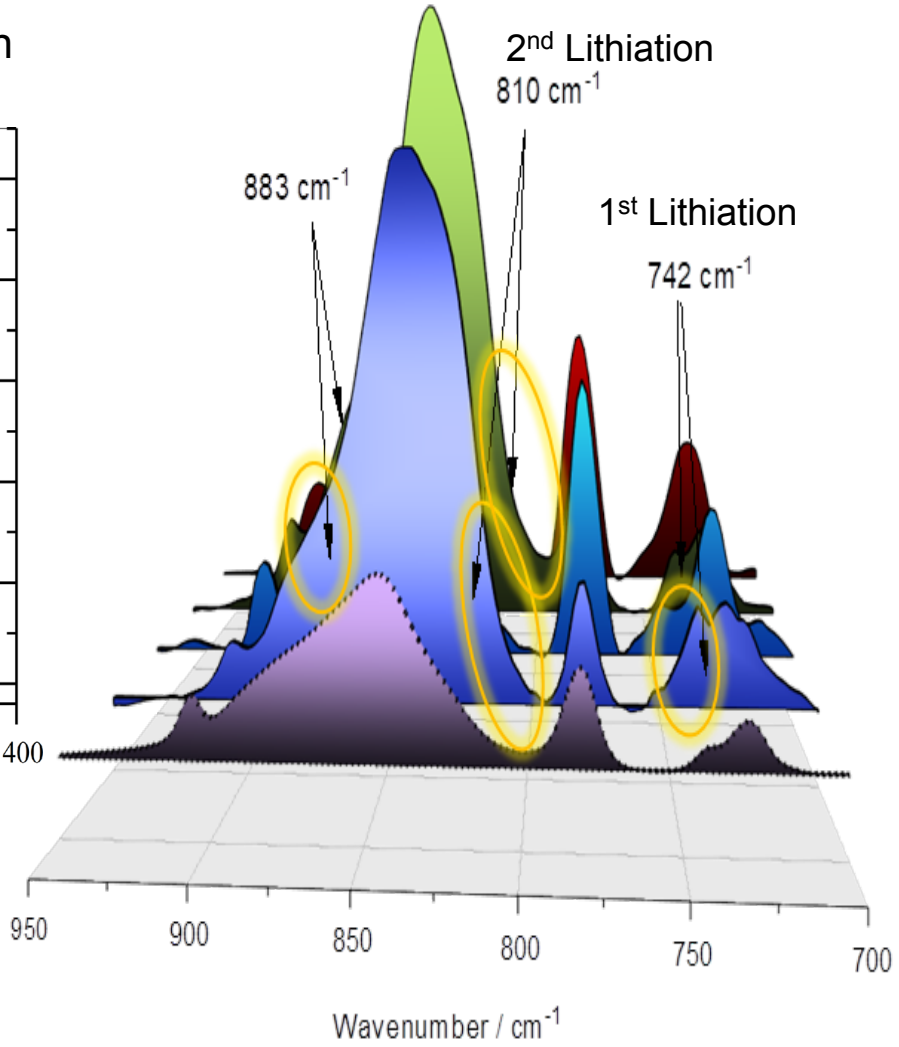
FTIR spectra of sputtered lithium silicates



Peak deconvolution of Li/Si=7.7 film



Coyle et al., J. Vac. Sci. Technol. A, 2017

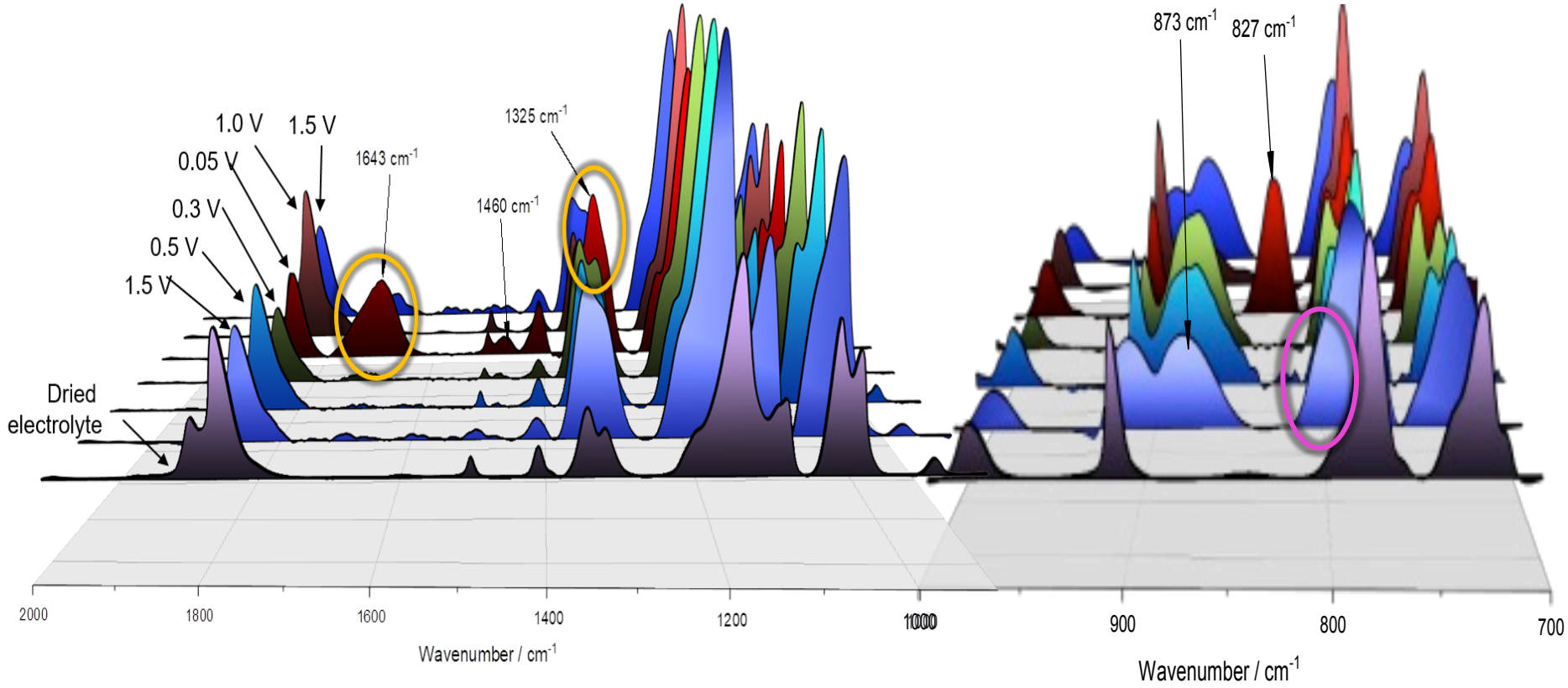


- The broadening of the peaks in the 800-900 cm^{-1} region may be associated with (i) accumulation of (P-F)-containing species, (ii) formation of solid solution silicates Li_xSiO_y.
- No obvious IR spectral signature of stoichiometric silicates.

Silicates in the SEI Layer of Si Anodes

Are Li_xSiO_y silicates involved in the SEI formation?

To separate possible interference from (P-F) containing species a series of measurements in 1.2M LiTFSI EC:EMC 3:7 wt.% was carried out



- LiEDC still observed on the Si electrode in 1.2M LiTFSI EC:EMC at 0.05 V
- Multiple bands in 740-950 cm^{-1} region may be associated with formation of solid solution silicates Li_xSiO_y.
- No direct spectroscopic evidence of stoichiometric silicates.

Summary

1. LiEDC and LiF constitute the main components of the SEI layer on the model thin-film Si electrode.
   - LiEDC forms at very low cathodic potentials (0.05 V) and then it disappears during the anodic scan.
   - This phenomenon can be directly related to the observed instability of the SEI layer on Si.
2. FTIR, XAS and neutron reflectometry measurements indicate a dynamic growth and dissolution of the SEI layer on Si electrodes during cycling. This SEI layer "breathing" presents a strong evidence of the instability of the SEI on Si and it could be directly linked to its inherent non passivating behavior.
3. Preliminary results confirm formation of non-stoichiometric solid solution Li_xSiO_y species, which may affect the chemical composition of the SEI layer. No direct spectroscopic evidence of stoichiometric silicates formation in the SEI.

This study not only determines the mechanism of the SEI formation on Si electrodes but also offer unique insights into its dynamic behavior during cycling.

Remaining Challenges and Barriers

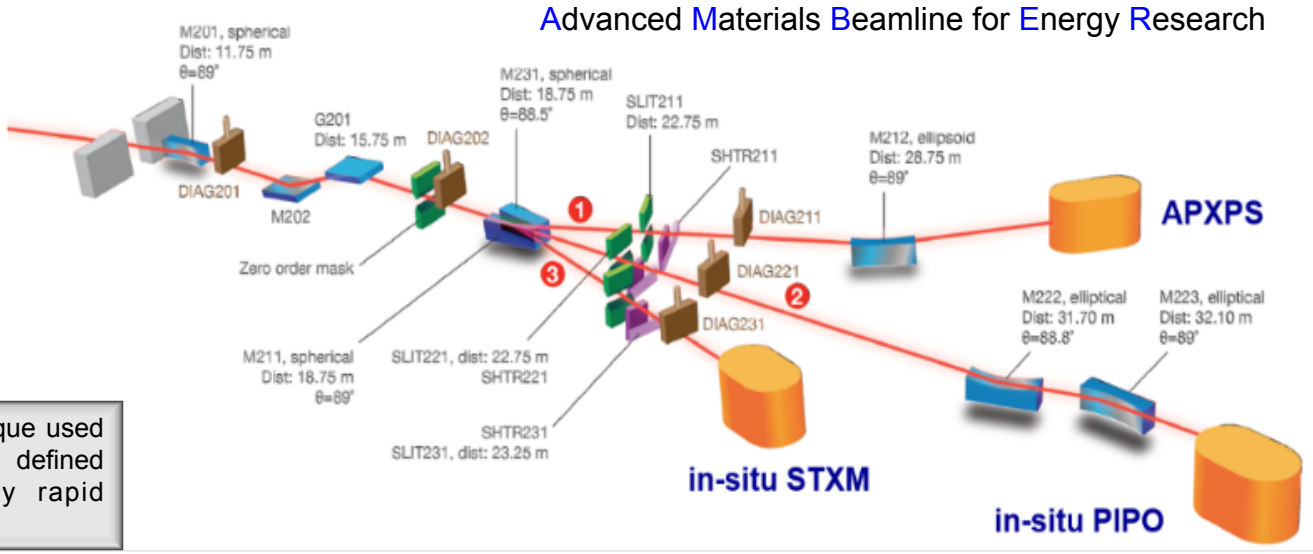
1. Large irreversible capacity loss and gradual electrolyte consumption and lithium inventory shift.
2. Inherent non-passivating behavior of intermetallic Li-ion anode materials in organic electrolytes.
   - Is the list of chemical compounds in the surface film complete?
   - What is the physical architecture of the film?
   - What is the exact (if any) function of all individual components?
   - Is the the surface film a solid electrolyte?

- *Develop new and unique analytical setups to probe and understand the function and operation of IM/electrolyte interfaces and interphases.*
- *Design and deploy new model IM (Si, Ge, Sn, Sb and their alloys.) electrodes.*

Future Work

- Develop new model electrodes for control and modification of physico-chemical properties
  - Complete installation and training on the new Splat Quencher machine. Carry out preliminary synthesis runs of selected Si-Me (Me = Sn, Al, Mn, Ti) amorphous binary and ternary glasses.
  - Obtain preliminary samples of amorphous silicon-Me alloys via splat quenching synthesis. Ship them to the other participating labs for preliminary evaluation.
- Correlate interfacial properties with electrochemical behavior and electrode performance challenges.
  - Develop a new *in situ* experimental setup for near-field FTIR and XAS measurements.
- Modify of model electrodes that successfully address performance challenge.
  - Design and study model electrodes with tailored interfaces to control the kinetics i.e., rate and selectivity of interfacial processes.

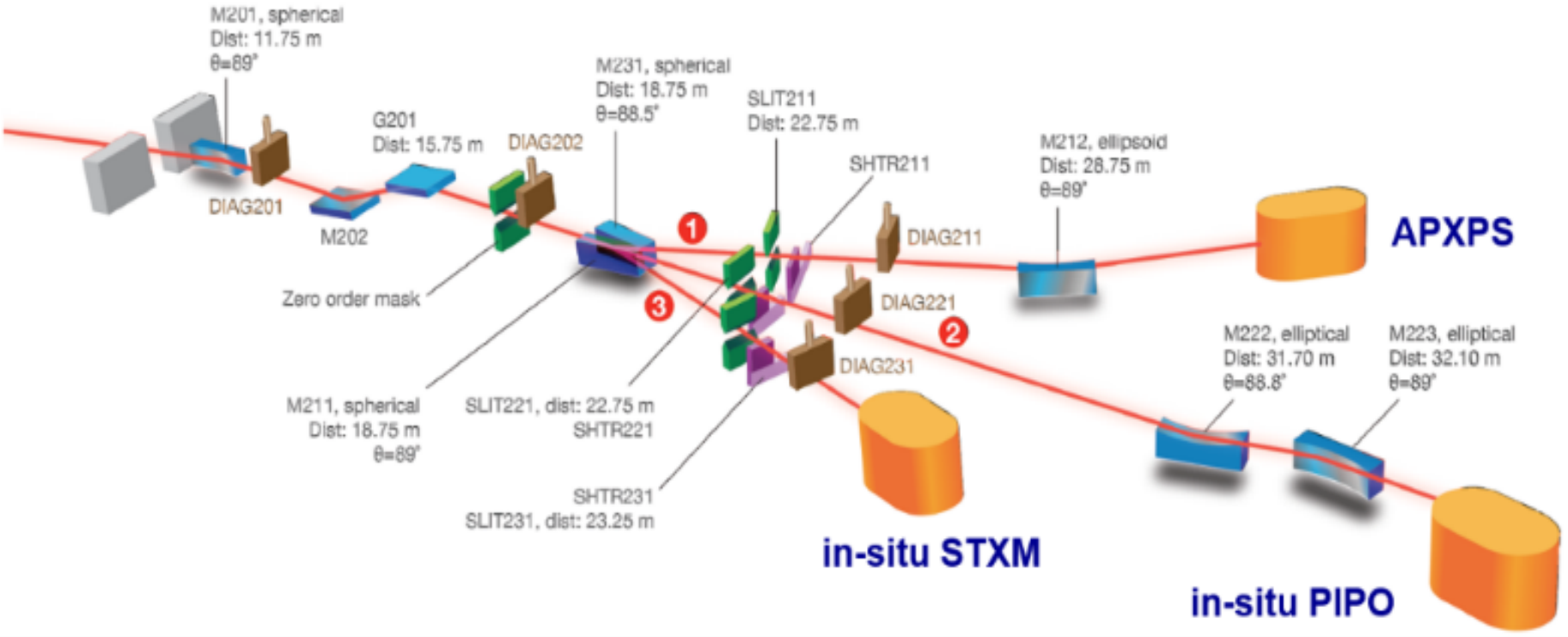
Splat quenching is a metallurgical technique used to form metals and metal alloys with a defined morphology by means of extremely rapid quenching, or cooling of molten metals.



Technical Backup Slides

Advanced Materials Beamline for Energy Research

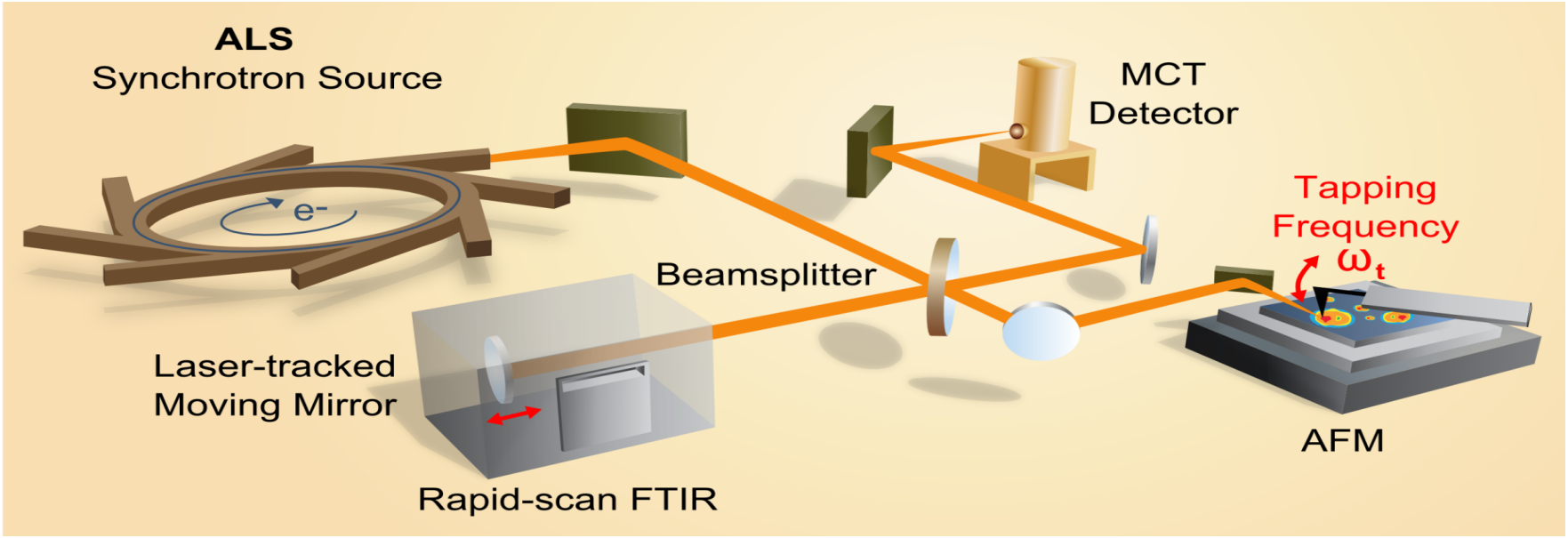
AMBER



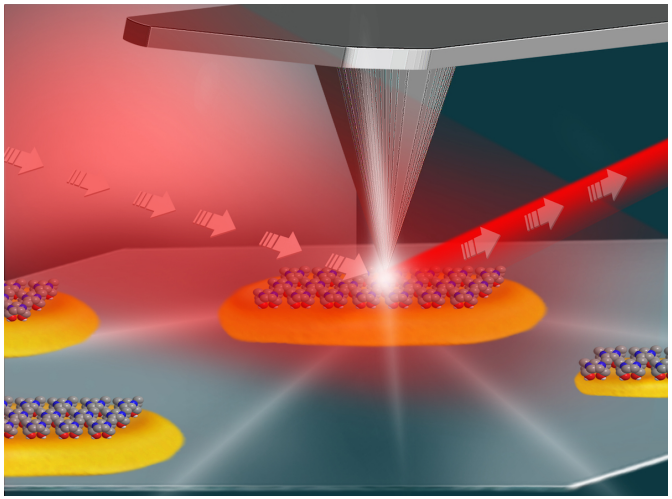
This new high-intensity, wide-energy-range (50-2500 eV) beamline and its three endstations are optimized for understanding and tailoring properties of novel materials that are suitable for energy conversion and energy storage.

LBNL ALS makes IR, too!

Near-Field Scanning Infrared Spectroscopy/Microscopy



Bechtel et al., PNAS, 111, 7191 (2014)



Using this synchrotron infrared nano-spectroscopy we achieve spectroscopic imaging with nanometer spatial resolution and high sensitivity that enables the investigation of nanoscale phenomena in energy storage model systems.